Novel Alkyne and Phosphaalkyne Coupling on an Ir_4 Cluster: Synthesis and Molecular Structure of $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$

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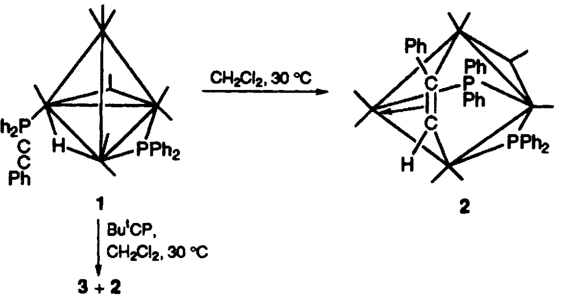
The cluster compound $[(\mu\text{-}H)Ir_4(CO)_9(Ph_2PCCPh)(\mu\text{-}PPh_2)]$ **1** reacts with the phosphaalkyne Bu^tCP to yield $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **3**, containing the novel 2-phosphabutadienylphosphine fragment as a result of the coupling of Bu^tCP with the diphenylphosphinoalkyne ligand and incorporation of the cluster bound H atom.

There are relatively few examples of controlled alkyne–alkyne coupling reactions at polynuclear carbonyl clusters.[1] The chemistry of phosphaalkynes, RCP, is of considerable contemporary interest and their similarity to alkynes has been stressed previously.[2] There is only one reported interaction between an alkyne and a phosphaalkyne, leading to a mononuclear η^4-1-phosphacyclobutadiene complex described by Binger *et al.*[3]

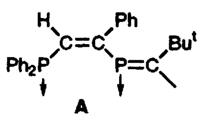
We recently reported that $[(\mu\text{-}H)Ir_4(CO)_9(Ph_2PCCPh)(\mu\text{-}PPh_2)]$ **1** containing a terminally bound diphenylphosphinoacetylene undergoes a facile rearrangement into $[Ir_4(\mu\text{-}CO)(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **2**, and it was proposed to occur *via* CO loss, $P\text{–}C_{sp}$ bond cleavage and hydride migration on to the α-carbon of the acetylide fragment.[4] Cluster coordinated acetylides have been shown to undergo nucleophilic attack of alkynes at the α-carbon[5,6] and in an attempt to trap the proposed hydrido–acetylido intermediate in the transformation of **1** into **2**, this reaction was carried out in the presence of Bu^tCP.

We report here the first example of a phosphaalkyne–alkyne coupling reaction in the coordination sphere of a cluster compound (Scheme 1), and describe the synthesis and characterization of $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **3**, which contains the 2-phosphabutadienylphosphine chain $\{Ph_2PC(H)C(Ph)PCBu^t\}$. Very recently, an attempt by Imhof and Huttner to couple similar molecules on a trinuclear iron phosphinidene carbonyl cluster led to very different products,[7] and although a number of 2-phosphabutadienes are known[8] none have previously been obtained by the alkyne–phosphaalkyne coupling route.

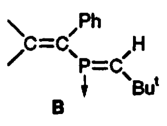
The reaction of cluster **1** with Bu^tCP in CH_2Cl_2 at 30 °C for 4 h resulted in a colour change from orange to dark brown and the formation of **3** in yields up to 40% [silica gel, CH_2Cl_2–hexane (3 : 7)]. Small amounts of compound **2** were unavoidably obtained, because of the competing rates of the two reactions. Compound **3** was formulated on the basis of spectroscopic and analytical data.† The coupling reaction between the Ph_2PCCPh ligand and the Bu^tCP molecule, and hydride migration to the resulting new phosphorus carbon chain were established by ^1H, ^{31}P and ^{13}C NMR spectroscopy. In spite of the detailed spectroscopic studies undertaken, it was impossible to establish unambiguously the position of the hydrogen atom in the chain, and whether the diphenylphosphinoalkyne had undergone $P\text{–}C_{sp}$ bond cleavage. A doublet of doublets pattern at δ 5.40 was observed in the ^1H NMR spectrum of **3** and the 2D H–P shift correlation spectrum indicated that the strong coupling of 54.6 Hz was to the P^2 nucleus (δ 8.6), while the 13.1 Hz coupling was to the PPh_2 phosphorus (P^1) (δ 20.5); the latter fragment could either be bound to the chain, as shown in **A**, or as a μ-PPh_2 ligand to the metal framework, **B**. In the first case, the *trans*-H to phosphaalkene P^2 arrangement would result in the large $^3J(H,P)$ observed. In the $^{31}P\{^1H\}$ NMR spectrum of **3**, the lowest field resonance (δ 109.2) was confidently attributed to the bridging phosphido P^3 nucleus, on the basis of previous work,[4] but, since the chemical shifts of μ-PPh_2 phosphorus nuclei have been shown to span a wide range and are



Scheme 1



A



B

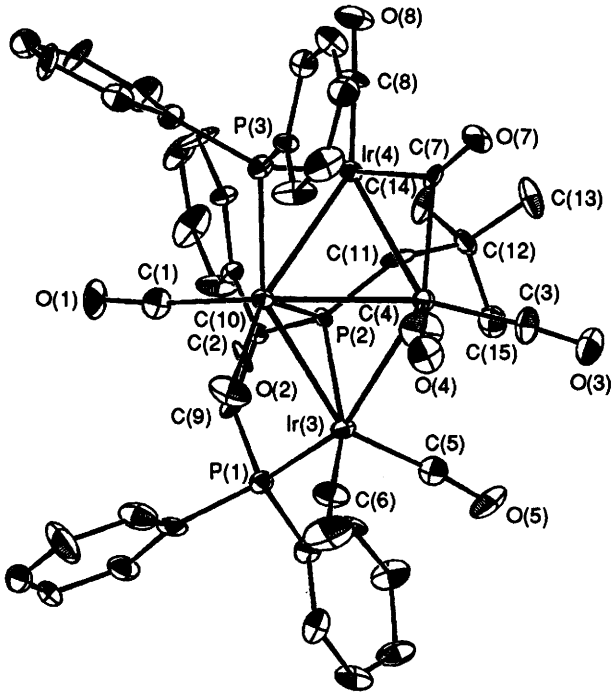


Fig. 1 Molecular structure of **3** (ORTEP showing the non-H atoms as 20% thermal vibration ellipsoids). Selected bond distances (Å) and angles (°): Ir(1)–Ir(2) 2.798(1), Ir(1)–Ir(3) 2.793(1), Ir(1)–Ir(4) 2.839(1), Ir(2)–Ir(3) 2.788(1), Ir(2)–Ir(4) 2.704(1), Ir(1)–P(2) 2.347(5), Ir(1)–P(3) 2.386(7), Ir(2)–P(2) 2.733(5), Ir(3)–P(1) 2.293(6), Ir(3)–P(2) 2.279(6), Ir(4)–P(3) 2.264(5), Ir(2)–C(11) 2.25(2), Ir(4)–C(11) 2.06(2), P(1)–C(9) 1.81(2), C(9)–C(10) 1.33(3), P(2)–C(10) 1.85(2), P(2)–C(11) 1.67(2); Ir(3)–P(1)–C(9) 107.4(7), Ir(3)–P(1)–C(16) 121.7(8), P(1)–C(9)–C(10) 124(2), P(2)–C(10)–C(9) 113(1), C(10)–P(2)–C(11) 125(1), P(2)–C(11)–C(12) 131(2).

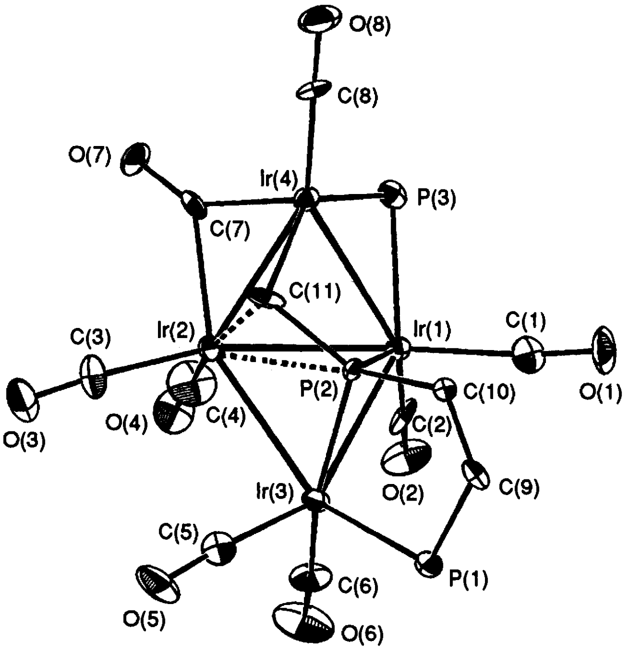
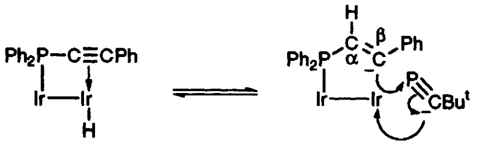


Fig. 2 Simplified view of **3** showing the 2-phosphabutadienylphosphine chain on the metallic framework; phenyl rings and the Bu^t group have been omitted for the sake of clarity



I **II**

dependent on the distance between the metal atoms they bridge,[9,10] the resonance at δ 20.5 could be alternatively assigned to a μ-PPh$_2$ phosphorus spanning two non-interacting iridium atoms. The proton on the phosphaalkene carbon would then be coupled with the nearest μ-PPh$_2$ ligand. The ^{13}C{^{1}H} NMR spectrum shows a doublet of doublets at δ 126.0 and the DEPT study indicates that this carbon is also bound to a proton. The results of these experiments support either structures **A** or **B**.

The molecular structure of **3** was determined by a single X-ray diffraction study (Fig. 1)‡ and confirmed the arrangement shown in **A**. It consists of the expected butterfly arrangement of iridium atoms previously observed for other 62-electron species,[10] with the longest and shortest edges [Ir(1)–Ir(4) 2.839(1) and Ir(2)–Ir(4) 2.704(1) Å], respectively, spanned by one phosphido and one carbonyl ligand. The other seven CO ligands are terminally bound to the iridium atoms. Interestingly, the C=C double bond [C(9)–C(10) 1.33(3) Å] of the 2-phosphabutadienylphosphine {Ph$_2$PC(H)C(Ph)PCBu^t} fragment does not interact at all with the metal framework, and likewise, the Ph$_2$P phosphorus binds only to Ir(3) [Ir(3)–P(1) 2.293(6) Å]. The 2-phosphaalkenyl P(2)=C(11) system, on the other hand, interacts with all four iridium atoms (Fig. 2), formally donating five electrons to the cluster, *via* two P(2)–Ir and one C(11)–Ir σ bonds [Ir(1)–P(2) 2.347(5) and Ir(3)–P(2) 2.279(6), and Ir(4)–C(11) 2.06(2) Å, respectively] and *via* a weak π-interaction [Ir(2)–P(2) 2.733(5) and Ir(2)–C(11) 2.25(2) Å]. Both the P–C distance [P(2)–C(11) 1.67(2) Å] and the C(10)–P(2)=C(11) and P(2)=C(11)–C(12) bond angles, [125(1) and 131(2)^0, respectively], indicate that the hybridization of the 2-phosphaalkenyl P and C atoms is essentially sp^2. A formal electron count results in 19 and 17 electrons on Ir(2) and Ir(4), respectively, and 18 electrons on the other two metal atoms.

Although no information regarding the detailed mechanism of the formation of **3** is available, it is interesting that, contrary to expectation, the product still contains an intact (Ph$_2$)P–C bond. If an equilibrium is operating between a cluster hydride–alkyne **I** and cluster alkenyl species **II**, nucleophilic attack of the β-carbon at the δ$^+$ P of the Bu^{t}CP molecule would yield the 2-phosphabutadienylphosphine observed.

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Footnotes

† *Spectroscopic data* for **3**: IR (hexane), (νCO) 2068w, 2058s, 2030vs, 2014w (sh), 2006s, 1985w, 1956s, 1836m cm^{-1}; FAB MS (nitrobenzylalcohol matrix) (calc. for ^{193}Ir), *m/z* 1567 (M)$^{\cdot+}$, 1567 − 28*x*, *x* = 1–8 [M − (CO)$_x$]$^{\cdot+}$; ^{1}H NMR, δ 1.08 [s, 9H; C(CH$_3$)$_3$], 5.40 [dd, 1H, ^3J(H,P) = 54.6 Bu^{t}CP, ^2J(H,P) = 13.1 Hz PPh$_2$], 7.19 – 7.71 (m, 25H, Ph); ^{31}P {^{1}H} NMR, δ 109.4, 20.5, 8.6 [pseudo-triplets *J*(P,P) = 10.7 Hz, μ-PPh$_2$, Ph$_2$PC and Bu^{t}CP, respectively]; ^{13}C{^{1}H} NMR, δ 191.17 [d, *J*(C,P) = 5.9 Hz, CO], 183.30 [d, *J*(C,P) = 73.5 Hz, CO], 175.50 [t, *J*(C,P) = 70.5 Hz, CO], 173.80 [d, *J*(C,P) = 48.8 Hz, CO], 170.40 (s), 167.97 [d, *J*(C,P) = 25 Hz, CO], 165.80 [d, *J*(C,P) = 110.8 Hz, CO], 161.80 (br), 141.75 [d, *J*(C,P) = 33 Hz, Ph], 138.44 [d, *J*(C,P) = 29.5 Hz, Ph], 135.96 [d, *J*(C,P) = 57 Hz, Ph], 134.80 [dd, *J*(C,P) = 8.0, 21.2 Hz, Ph], 133.74 [d, *J*(C,P) = 13.2 Hz, Ph], 132.65 [d, *J*(C,P) = 11.6 Hz, Ph], 132.06 [d, *J*(C,P) = 13.0 Hz, Ph], 131.71 (s, Ph), 130.56 (s, Ph), 130.15 (s, Ph), 129.89 (s, Ph), 129.65 [t, *J*(C,P) = 19.3 Hz, Ph], 129.14 [d, *J*(C,P) = 11.0 Hz], 128.64 [d, *J*(C,P) = 12 Hz, Ph], 128.28 [*t*, *J*(C,P) = 25.6 Hz, Ph], 126.00 [dd, *J*(C,P) = 34.8, 57.3 Hz, CH], 54.17 [dd, *J*(C,P) = 27.8, 37.1 Hz], 38.50 [s, C(CH$_3$)$_3$], 33.64 [d, *J*(CP) = 7.9 Hz, CH$_3$], 29.64 (s); correct elemental analysis for $C_{45}H_{35}Ir_4O_8P_3$.

‡ X-ray crystal structure analysis of **3** at 273 K; $C_{45}H_{35}Ir_4O_8P_3 \cdot CHCl_3$, monoclinic, space group *C2/c*, *a* = 41.913(8), *b* = 12.747(4), *c* = 18.522(5) Å, β = 95.17(2)°, *Z* = 8. μ(Mo-Kα) = 110.4 cm^{-1}, CAD4. 9081 measured reflections, 5465 with $|F^2|$ 2σ(F^2); *R* = 0.066, R_w = 0.064 [$w = 1/\sigma^2 (F_o)$] for 577 parameters.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203; J. R. Shapley, C. H. McAteer, M. R. Churchill and L. V. Biondi, *Organometallics*, 1984, **3**, 1595; V. Riaz, M. D. Curtis, A. Rheingold and B. S. Haggerty, *Organometallics*, 1990, **9**, 2647; H. Matsuzaka, Y. Mizobe, M. Nishio and M. Hidai, *J. Chem. Soc., Chem. Commun.*, 1991, 1011.
2 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327; *Chem. Ind.* 1993, 404.
3 P. Binger, R. Milczarek, R. Mynott and M. Regitz, *J. Organomet. Chem.*, 1987, **323**, C35.
4 M. H. A. Benvenutti, D. Braga, F. Grepioni, B. E. Mann, S. Naylor and M. D. Vargas, *Organometallics*, 1993, **12**, 2947.
5 E. Sappa, G. Pasquinelli, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1989, 601 and references therein.
6 Y. Chi, D.-K. Hwang, S.-F. Chen and L.-K. Liu, *J. Chem. Soc., Chem. Commun.*, 1989, 1540; Y. Chi, G. Huttner and W. Imhof, *J. Organomet. Chem.*, 1990, **384**, 93.
7 W. Imhof and G. Huttner, *J. Organomet. Chem.*, 1993, **447**, 31.
8 R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990.
9 A. J. Carty, S. A. MacLaughlin and D. Nucciarone, in *Phosphorus 31 NMR Spectroscopy in Stereochemical Analysis, Organic Compounds and Metal Complexes*, ed. J. G. Verkade and L. D. Quinn, VCH, New York, 1987, ch. 16.
10 M. H. A. Benvenutti, D. Braga, F. Grepioni, B. E. Mann, E. Parisini and M. D. Vargas, *Organometallics*, 1993, **12**, 2955; D. Braga, F. Grepioni, R. M. S. Pereira and M. D. Vargas, *J. Chem. Soc. Chem. Commun.*, 1993, 1008.